

(11) **EP 1 067 595 A3**

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3: 16.01.2002 Bulletin 2002/03

(51) Int Cl.7: C23C 16/40, C23C 16/34

(43) Date of publication A2: 10.01.2001 Bulletin 2001/02

(21) Application number: 00114321.3

(22) Date of filing: 04.07.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 08.07.1999 US 350074

(71) Applicant: AIR PRODUCTS AND CHEMICALS, INC.
Allentown, PA 18195-1501 (US)

(72) Inventors:

- Senzaki, Yoshihide Carlsbad, CA 92009 (US)
- Roberts, David Allen Encinitas, CA 92024 (US)
- Norman, John Anthony Thomas Encinitas, CA 92024 (US)
- (74) Representative: Kador & Partner Corneliusstrasse 15 80469 München (DE)

(54) Liquid precursor mixtures for deposition of multicomponent metal containing materials

(57) The present invention is a composition for deposition of a mixed metal or metal compound layer, comprising a solventless mixture of at least two metal-ligand complex precursors, wherein the mixture is liquid at ambient conditions and the ligands are the same and are selected from the group consisting of alkyls, alkoxides, halides, hydrides, amides, imides, azides cyclopentadienyls, carbonyls, and their fluorine, oxygen and nitrogen substituted analogs. The present invention is also a process for deposition of a multiple metal or metal compound layer on a substrate of an electronic material, comprising: a) providing a solventless mixture of two or

more metal-ligand complex precursors which constitute a liquid at ambient conditions, wherein the ligands are the same and are selected from the group consisting of alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, and their fluorine, oxygen and nitrogen substituted analogs; b) delivering the solventless mixture by direct liquid injection to a flash vaporization zone to vaporize the solventless mixture; c) contacting the substrate under deposition conditions with a resulting vapor of the solventless mixture, and c) depositing a multiple metal or metal compound layer on the substrate from the solventless mixture.



EPO FORM 1503 03.82 (P04C01)

EUROPEAN SEARCH REPORT

Application Number EP 00 11 4321

	DOCUMENTS CONSID	ERED TO BE RELEVANT		
Category	Citation of document with of relevant pas	ndication, where appropriate, sages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InLCI.7)
X Y	US 3 632 429 A (MAE 4 January 1972 (197 * column 3, line 42	(2-01-04)	1,9,10, 12,13 2-6	C23C16/40 C23C16/34
X Y	23 May 1995 (1995-0	RICQ MICHEL M ET AL) 05-23) line 61; example 4 *	1,10,11, 13,14 2,7,8	
K	PATENT ABSTRACTS OF vol. 009, no. 254 (11 October 1985 (19 & JP 60 108338 A (N KOSHA), 13 June 198	C-308), 085-10-11) HIPPON DENSHIN DENWA	1	
A	* abstract *		10,14, 17,19	
Y	US 5 464 666 A (FIN 7 November 1995 (19	E STEPHEN M ET AL)	2-8	
A	* examples 3,4 *		10,11,13	"
A,D	US 5 204 314 A (GAR 20 April 1993 (1993 * column 9, line 26	DINER ROBIN A ET AL) 3-04-20) 5-11ne 37 *	1-21	TECHNICAL FIELDS SEARCHED (Int.CI.7)
A	10 June 1999 (1999- * page 2, line 23 -		1-21	B29F
A	US 5 262 199 A (DES 16 November 1993 (1 * claims 20-24 *		19	
		-/		
	The present search report has	been drawn up for all claims		
	Place of search THE HAGUE	Date of completion of the search 16 November 2001	Ekh	Examiner ult, H
X : parti Y : parti docu A : tech O : non-	ATEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with and iment of the same category nological background written disclosure mediate document	T: theory or principle E: earlier patent doc after the filling date	e underlying the later than the sument, but public en the application or other reasons	nvention shed on, or

2



Application Number

EP 00 11 4321

CLAIMS INCURRING FEES
The present European patent application comprised at the time of filing more than ten claims.
Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.
LACK OF UNITY OF INVENTION
The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:
see sheet B
All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
As all searchable claims could be searched without effort justifying an additional tee, the Search Division did not invite payment of any additional fee.
Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



EUROPEAN SEARCH REPORT

Application Number EP 00 11 4321

		RED TO BE RELEVANT		
Category	Citation of document with in of relevant passa		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	LOW-TEMPERATURE ATMOCHEMICAL VAPOR DEPOSILICON OXIDE THIN FOR CHEMISTRY OF MATERIA SOCIETY, WASHINGTON,	INDS AS PRECURSORS FOR OSPHERIC PRESSURE SITION OF TIN AND FILMS" ALS, AMERICAN CHEMICAL US, 11 1994 (1994-04-01), 0483694	15,16	
A	DATABASE WPI Section Ch, Week 199 Derwent Publications Class LO3, AN 1999-2 XP002183078 & JP 11 074478 A (MACORP), 16 March 1999 * abstract *	ttd., London, GB; 50898 TSUSHITA ELECTRONICS	18,20	TECHNICAL FIELDS SEARCHED (Int.C1.7)
A		-04) - column 3, line 51 *	21	
	The present search report has be	Date of completion of the search	<u> 1</u>	Examiner
	THE HAGUE	16 November 2001	Ekhu	ilt, H
X : parti Y : parti docu	ATEGORY OF CITED DOCUMENTS cularly relevant if taken atone cularly relevant if combined with anothe ment of the same category now product of the same category new parties of the same category white category whit	L : document cited f	cument, but publis ite in the application or other reasons	hed on, or

4



LACK OF UNITY OF INVENTION SHEET B

Application Number

EP 00 11 4321

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-10,13

Processes and composition for deposition of a multiple metal or metal compound layer on a substrate of an electronic material, comprising using a solventless mixture of two or more metal-ligand complex precursors which constitute a liquid at ambient conditions, wherein said ligands are selected from the group consisting of alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, and their fluorine, oxygen and nitrogen substituted analogs.

2. Claims: 10,11

Solventless mixture of at least two metal-ligand complex precursors, wherein said mixture is liquid at ambient conditions and said ligands are selected from the group consisting of alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, and their fluorine and oxygen and nitrogen substituted analogs, and a first metal-ligand complex precursor which is liquid at ambient conditions and a second metal-ligand complex precursor which is liquid at ambient conditions.

3. Claims: 10,12

Solventless mixture of at least two metal-ligand complex precursors, wherein said mixture is liquid at ambient conditions and said ligands are selected from the group consisting of alkyls, alkoxides, halides, hydrides, amides, imides, azides, nitrates, cyclopentadienyls, carbonyls, pand their fluorine and oxygen and nitrogen substituted analogs, and a first metal-ligand complex precursor which is liquid at ambient conditions and a second metal-ligand complex precursor which is solid at ambient conditions and miscible in the first metal-ligand complex precursor.

4. Claims: 10,14(partly)-16,18,20,21

A solventless mixture of at least two metal-ligand complex precursors said mixture is liquid at ambient conditions, the ligand being selected from the group dimethyl amido, diethyl amido, ethylmethyl amido, butyl amido, dipropyl amido, methylpropyl amido, ethylpropyl amido.

5. Claims: 10,14(partly),17,19



LACK OF UNITY OF INVENTION SHEET B

Application Number

EP 00 11 4321

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

A solventless mixture of at least two metal-ligand complex precursors said mixture is liquid at ambient conditions, the ligand being selected from the group methoxy, ethoxy, propoxy, and butoxy.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 00 11 4321

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-11-2001

Patent document cited in search rep		Publication date		Patent farr member(Publicatio date
3632429	A	04-01-1972	NONE			
5417823	A	23-05-1995	NONE			
60108338	Α	13-06-1985	NONE			
5464666	Α	07-11-1995	DE			08-08-199
						07-08-199
			JP 	8319566	A 	03-12-199
5204314	Α	20-04-1993	AT			15-04-199
						24-06-199
					_	07-05-199
						30-07-199
						19-10-199
						28-09-199
						16-06-199
						20-04-199
						16-08-199
						24-06-199
						08-11-199
						16-07-199
						11-07-199
						13-10-199
			-			24-11-199 27-01-199
					• •	29-08-200
						05-07-200
						03-10-200
						26-09-199
						17-04-200
						06-07-199
			US			18-01-199
9928051	Δ	10-06-1999	IIS	6045864	Α	04-04-200
7920031	Α	10 00 1333				20-09-200
						10-06-199
			ÜS			12-06-200
5262199	Α	16-11-1993	MO	9321358	A1	28-10-199
3202199						
11074478	A	16-03-1999	NONE			
	5417823 60108338 5464666	5417823 A 60108338 A 5464666 A 5204314 A	5417823 A 23-05-1995 60108338 A 13-06-1985 5464666 A 07-11-1995 5204314 A 20-04-1993	5417823 A 23-05-1995 NONE 60108338 A 13-06-1985 NONE 5464666 A 07-11-1995 DE GB JP 5204314 A 20-04-1993 AT CA DE	5417823 A 23-05-1995 NONE 60108338 A 13-06-1985 NONE 5464666 A 07-11-1995 DE 19603282 GB 2297560 JP 8319566 5204314 A 20-04-1993 AT 164632 CA 2125657 DE 69224996 DE 69224996 DE 69224996 DE 69224996 DE 52 2115048 JP 7503759 US 5337651 WO 9312266 US 5362328 US 5536323 US 5431957 US 5840897 US 5711816 US 6110529 US 2001007034 US 6126996 US 5453494 US 6218518 US 5225561 US 5280012 9928051 A 10-06-1999 US 6045864 EP 1035927 WO 9928051	5417823 A 23-05-1995 NONE 60108338 A 13-06-1985 NONE 5464666 A 07-11-1995 DE 19603282 A1 GB 2297560 A , B JP 8319566 A 5204314 A 20-04-1993 AT 164632 T CA 2125657 A1 DE 69224996 D1 DE 69224996 T2 DK 616649 T3 EP 0616649 A1 ES 2115048 T3 JP 7503759 T US 5337651 A W0 9312266 A1 US 5362328 A US 55362328 A US 55362328 A US 55362328 A US 55362328 A US 5711816 A US 5840897 A US 5711816 A US 6110529 A US 543494 A US 6218518 B1 US 5225561 A US 5280012 A 9928051 A 10-06-1999 US 6045864 A EP 1035927 A1 W0 9928051 A1